

**REMARKS/ARGUMENTS**

Reconsideration of the above-identified application is respectfully requested.

In the Office Action dated November 24, 2008, the Examiner indicated that claims 19-32 were withdrawn from consideration. The Examiner alleged that “[n]ewly submitted claims 19-32 are directed to an invention that is independent or distinct from the invention originally claimed for the following reasons: Original claims were drawn to a powder, a product containing the powder and various uses of the powder on skin, the newly added claims are product by process and method of making claims.”

Applicants respectfully traverse the Examiner’s unilateral decision to withdraw claims 19-32. There has been no restriction requirement in the case to require Applicants to elect claims drawn to separate classes. Also, product by process claims are still product claims, which belong to the same class of claims drawn to the products. Withdrawal of the decision to withdraw claims 19-32 is therefore respectfully requested.

Claims 2, 4, 5 and 15-17 are rejected under 35 U.S.C. §102(b) as being anticipated by JP05-058624 (hereinafter “JP624”).

Claims 2, 4, 5 and 15 are rejected under 35 U.S.C. §103(a) as being unpatentable over Bloom et al. (hereinafter “Bloom”) in view of CA2,374,539 (hereinafter “CA539”).

Claims 2, 4, 5 and 15-17 are rejected under 35 U.S.C. §103(a) as being unpatentable over JP624 in view of US6,632,276 (hereinafter “US276”).

Applicants respectfully submit that Claims 2, 4, 5 and 15-17 are patentable over the cited prior art references for the reasons set forth below:

**Rejections under 35 U.S.C. §102**

Claims 2, 4, 5 and 15-17 are rejected under 35 U.S.C. §102(b) as being anticipated by JP624. Applicants respectfully reverse the rejections for the following reasons.

For anticipation under 35 U.S.C. §102, the reference “must teach every aspect of the claimed invention either explicitly or impliedly. Any feature not directly taught must be inherently present.” See MPEP §706.02, IV. The Federal Circuit has consistently held that prior art is anticipatory only if every element of the claimed invention is disclosed in a single item of prior art in the form literally defined in the claim. See e.g., *Jamesbury Corp. v. Litton Indus. Products*, 756 F.2d 1556, (Fed. Cir. 1985); *Atlas Powder Co. v. DuPont*, 750 F.2d 1569, (Fed. Cir. 1984); *American Hospital Supply v. Travenol Labs*, 745 F.2d 1 (Fed. Cir. 1984).

Independent claim 2 of the instant application, as amended, is directed to “an insoluble powder having a negative value of zeta-potential and a main ingredient of barium sulfate doped with a metal ion, wherein said powder has an average primary particle diameter of 3 to 100  $\mu\text{m}$  and an aspect ratio of 3 to 250, and wherein said metal ion is one selected from the group consisting of lithium, sodium and zinc.”

The specification explicitly teaches that barium sulfate and barium sulfate doped sulfate are made from different methods. In particular, the specification teaches that a powder of barium sulfate is prepared by a conventional two-solution method such as a method of mixing a barium compound solution containing a barium ion and a sulfate compound solution containing a sulfate ion at a reaction temperature of 50 to 100°C. The barium compound can be barium hydroxide, barium chloride, barium sulfide, barium

nitrate, or barium acetate. The sulfuric compound can be sulfuric acid, sodium sulfate, sodium hydrogensulfate, ammonium sulfate, potassium sulfate, lithium sulfate. (*See e.g.*, paragraphs [0047]-[0049]).

The Specification then teaches that the powder of barium sulfate doped with a metal is prepared by reacting a barium ion with a sulfate ion in the presence of a metal ion using a two-step, three-solution method. For example, the doped barium sulfate is obtained by mixing (A) a barium compound solution containing a barium ion with (B) a metal salt compound solution containing a doping ion and, thereafter, adding (C) a sulfate compound solution containing a sulfate ion to the mixture of A and B. Alternatively, doped barium sulfate is obtained by mixing A and C, and then add B to the mixture. (*See, e.g.*, paragraphs [0053]-[0058]).

Therefore, the specification explicitly teaches that the one-step, two-solution method only produces barium sulfate, but not doped barium sulfate.

On the other hand, JP624 describes a barium sulfate powder produced by the one-step, two-solution method using exactly the same chemicals and conditions referred to as the “conventional” method for making barium sulfate, rather than barium sulfate doped sulfate, as disclosed in the present application. Specifically, JP624 describes a method for making barium sulfate by mixing a solution of barium hydroxide, barium chloride, barium nitrate, or barium acetate (*cf* paragraph [0048] of the present application) with a solution of sulfuric acid, sodium sulfate, sodium hydrogensulfate, or ammonium sulfate (*cf* paragraph [0048] of the present application) at 60-100 °C (*cf* paragraph [0047] of the present application) (*See, e.g.*, claim 2 of machine translated JP624, attached hereto as Exhibit 1, and paragraphs [0006] and [0011]). Therefore, it is clear that the JP624

method produces barium sulfate, but not the doped barium sulfate as recited in the amended claim 2. Under current Federal Circuit precedents, it is improper to read claims on material which has been disparaged from the Specification. See e.g., *Inpro II Licensing, S.A.R.L. v. T-Mobile USA, Inc.*, 450 F.3d 1350, 1354 (Fed. Cir. 2006)(affirming district court's construction of "host-interface" as "a direct parallel bus interface" where, *inter alia*, the background of the specification disparaged serial-bus interfaces). That is because "[w]here the specification makes clear that the invention does not include a particular feature, that feature is deemed to be outside the reach of the claims of the patent, even though the language of the claims, read without reference to the specification, might be considered broad enough to encompass the feature in question." *SciMed Life Sys., Inc. v. Advanced Cardiovascular Sys., Inc.*, 242 F.3d 1337, 1341 (Fed. Cir. 2001). Although claims need not be limited to the preferred embodiment when the invention is more broadly described, "neither do the claims enlarge what is patented beyond what the inventor has described as the invention." *Netword, LLC v. Centraal Corp.*, 242 F.3d 1347, 1352 (Fed. Cir. 2001).

Therefore, the Examiner cannot arbitrarily assert, against the explicit teachings of the instant application, that the claimed doped barium sulfate includes the barium sulfate of JP624.

In response to Applicants' argument in the Response filed on September 12, 2008, the Examiner cites to MPEP 2113, which provides:

The patentability of a product does not depend on its method of production. If the product in the product-by-process claim is the same as or obvious from a product of the prior art, the claim is unpatentable even though the prior product was made by a different process."

Applicants would like to bring to the Examiner's attention that claim 2 is not a product-by-process claim. On the contrary, claim 2 simply claims a composition containing doped barium sulfate which, based on the explicit teachings in the specification, cannot be produced by the method described in JP624. In other words, the term "doped barium sulfate" in claim 2, would exclude the barium sulfate of JP624 because the instant specification explicitly teaches that the JP624 method produces barium sulfate but not doped barium sulfate.

Moreover, the JP '624 patent fails to disclose a barium sulfate powder having a negative value of zeta-potential as recited in claim 2. The Examiner maintains that the "negative zeta-potential" does not give it patentable weight, since "it is the same powder of the same size" See Office Action at 7. First, as discussed above, the barium sulfate of JP624 is not the "same powder" as the doped barium sulfate of instant claim 2. Further, even assuming that the JP624 barium sulfate is a doped barium sulfate, Applicants fail to perceive how the Examiner come to the conclusion that the JP624 barium sulfate would have a negative zeta potential just because the JP624 barium sulfate fall within the claimed size range. A person of ordinary skill in the art would understand that zeta potential is an electrical characteristic not directly related to the size of a particle, not to mention that the instant application has shown in Tables 1 and 2 that doped barium sulfate powder may have different zeta-potentials.

Accordingly, Applicants respectfully submit that claim 2 is not anticipated by the JP624, because JP624 fails to teach every aspect of the claimed invention. Applicants further submit that claims 4, 5, 15-17 are patentable over JP624 because they depend upon claim 2 and recite additional patentable subject matter. Withdrawal of the rejection

under 35 U.S.C. §102 is respectfully requested.

**Rejections under 35 U.S.C. §103**

Claims 2, 4, 5 and 15 are rejected under 35 U.S.C. §103(a) as being unpatentable over Bloom in view of CA539. Claims 2, 4, 5 and 15-17 are rejected under 35 U.S.C. §103(a) as being unpatentable over JP624 in view US276. Applicants respectfully traverse the rejections.

To establish a *prima facie* case of obviousness ... the prior art reference (or references when combined) must teach or suggest all of the claim limitations. *In re Vaeck*, 947 F.2d 488 (Fed. Cir. 1991) and *MPEP* § 2142.

Independent claim 2 of the present claimed application, as amended, is directed to an insoluble powder having a negative value of zeta-potential and main ingredient of barium sulfate doped with a metal ion, wherein said powder has an average primary particle diameter of 3 to 100  $\mu\text{m}$  and an aspect ratio of 3 to 250, and wherein said metal ion is one selected from the group consisting of lithium, sodium and zinc.

With respect to the rejections over Bloom and the CA '539 patent, Bloom generally describes alkali-metal interaction with trapped hydrogen atoms in barium sulfate. Bloom does not teach or suggest a barium sulfate powder having a negative value of zeta-potential and an aspect ratio of 3 to 250, as recited in claim 2.

As discussed in the Response filed on September 12, 2008, the doped barium sulfate of Bloom was prepared using a process that is different from the process described in the instant invention. Therefore, the barium sulfate of Bloom will not inherently have a negative value of zeta-potential and an aspect ratio of 3 to 250, as recited in claim 2. Since Applicants have explicitly taught in the specification that doped barium sulfate may

have different zeta-potential and different aspect ratio (*see, e.g.*, Tables 1 and 2), there is no basis for the Examiner to assert that the doped barium sulfate of Bloom would have the claimed zeta-potential and aspect ratio range.

CA539 does not cure the deficiency of Bloom. CA539 patent generally describes an anticorrosive comprising barium sulfate doped with tin or antimony as conductivity pigment or conductive filler. CA539 does not mention anything about the zeta potential and aspect ratio. Since it is well known in the art that barium sulfate powder may be produced in different shapes (*e.g.*, spherical, fir-like, plate-like, etc. ), the barium sulfate of the CA539 does not inherently possesses “a negative zeta potential” and “an aspect ratio of 3 to 250.” Therefore claim 2 is patentable over Bloom and CA539.

As discussed earlier, JP624 also fails to teach or suggest a doped barium sulfate, let alone doped barium sulfate with “a negative zeta potential” and “an aspect ratio of 3 to 250.” Specifically, US276 only mentions suspending barium sulfate particles in water and adding a water-soluble tin salt and a water-soluble phosphorus compound. A person of ordinary skill in the art would understand that this process will not convert non-doped barium sulfate to metal doped barium sulfate. Further, US276 only mentions a mixture of platelet-shaped and spherical particles. US276 does not teach or suggest “an aspect ratio of 3 to 250.” Finally, US276 is silent on zeta potential. Applicants again remind the Examiner that instant claim 2 is directed to a composition containing a doped barium sulfate with unique physical (aspect ratio) and electrical (zeta potential) characteristics that confers unexpected skin treating effect to the claimed composition. Since Applicants have explicitly taught in the specification that doped barium sulfate may come with different zeta-potential and different aspect ratio (*see, e.g.*, Tables 1 and 2), there is no

basis for the Examiner to assert that the doped barium sulfate of US276 would have the claimed zeta-potential and aspect ratio range, especially in view of the teachings in US276 itself that the barium sulfate particles disclosed therein may be either spherical or platelet-shaped. Therefore, claim 2 is patentable over JP624 and US276.

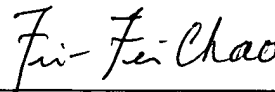
Taken together, Applicants respectfully submit that claim 2 is patentable over all the cited references and combinations of references because none of these references or combinations of references teach or suggest all claim limitations. Applicants further submit that claims 4, 5, 15-17 are patentable over the cited references because they depend from claim 2 and recite additional patentable subject matter. Withdrawal of the rejections under 35 U.S.C. §103 is respectfully requested.

#### **Conclusion**

In view of the above remarks, Applicant respectfully submits that the application is in condition for allowance. Prompt examination and allowance are respectfully requested.

Should the Examiner believe that anything further is desired in order to place the application in even better condition for allowance, the Examiner is invited to contact Applicant's undersigned representative at the telephone number listed below.

Respectfully submitted,



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Appl. No. 10/509,539  
Response dated May 15, 2009  
Reply to Office Action of November 24, 2008

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Enclosure: Exhibit 1: Machine translation of JP05-058624

Exhibit 1

(19)日本国特許庁(JP)

(12) 公開特許公報(A)

(11)特許出願公開番号

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(54)【発明の名称】 硫酸バリウムの製造方法

(57)【要約】

【構成】 バリウム化合物と硫酸化合物とを下記(a)～(c)の条件下で反応させることによる硫酸バリウムの製造方法。

(a) 0.001～0.1mol/lのバリウム化合物溶液及び硫酸化合物溶液を、バリウム化合物と硫酸化合物のモル比0.1～5で反応させる。

(b) バリウム化合物溶液及び硫酸化合物溶液のいずれか一方を他方に加える滴下時間を2秒～7分とする、

(c) 反応系のpHを0.5～1.0とする。

【効果】 本発明によれば、平均粒径が4から20μmと粗大で、光散乱強度が50%以上、かつ、光全透過率が70%以上の物性を有する硫酸バリウムが、安定して製造可能で、かかる粉体は使用感、隠ぺい性に優れ、高い光散乱性と透明性を有する化粧品用体質顔料として有用である。

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熱したバリウム溶液を2分間で投入した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは1.5から7.0であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末4.5gを得た。こうして得られた粉末は、平均粒径が4.5μmであり、光散乱強度60.3%、光全透過率88.7%であった。また、化粧料であるファンデーションに配合したところ、従来のマイカ、タルク等の体質顔料を配合したものに比べて、使用感が良好であり、化粧膜の透明性も高かった。

#### 【0016】実施例3

特級試薬 塩化バリウム2.08gと特級試薬 硫酸0.98gをイオン交換水2000gにそれぞれ溶解し、0.005mol/lのバリウム溶液と0.005mol/lの硫酸溶液とした。次に、5lフラスコに硫酸溶液を仕込み、テフロン製バドルにて200rpmで攪拌、80℃まで加熱後、80℃に加熱したバリウム溶液を10秒で投入した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは2から2であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.2gを得た。こうして得られた粉末は、平均粒径が8.5μmであり、光散乱強度62.4%、光全透過率90.5%であった。また、化粧料であるファンデーションに配合したところ、従来のマイカ、タルク等の体質顔料を配合したものに比べて、使用感が良好であり、化粧膜の透明性も高かった。

#### 【0017】実施例4

特級試薬 塩化バリウム8.32gと特級試薬 硫酸0.98gをイオン交換水1000gにそれぞれ溶解し、0.04mol/lのバリウム溶液と0.01mol/lの硫酸溶液とした。次に、2lフラスコにバリウム溶液を仕込み、テフロン製バドルにて200rpmで攪拌、100℃まで加熱後、100℃に加熱した硫酸溶液を30秒で投入した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは7から2であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.2gを得た。こうして得られた粉末は、平均粒径が6.4μmであり、光散乱強度61.5%、光全透過率87.3%であった。また、化粧料であるファンデーションに配合したところ、従来のマイカ、タルク等の体質顔料を配合したものに比べて、使用感が良好であり、化粧膜の透明性も高かった。

#### 【0018】実施例5

特級試薬 水酸化バリウム1.71gと特級試薬 硫酸0.98gをイオン交換水1000gにそれぞれ溶解し、0.01mol/lのバリウム溶液と0.01mol/lの硫酸溶液とした。次に、2lフラスコにバリウム溶液を仕込み、テフロン製バドルにて200rpmで攪拌、100℃まで加熱後、100℃に加熱した硫酸溶液を5分間で滴下した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは1.3で一定であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.2gを得た。こうして得られた粉末は、平均粒径が3.2μmであり、光散乱強度41.9%、光全透過率89.3%であった。また、化粧料であるファンデーションに配合したところ、使用感が悪く、光散乱性の悪い粉体であり、化粧料としては劣っていた。

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液を仕込み、テフロン製バドルにて200rpmで攪拌、60℃まで加熱後、60℃に加熱したバリウム溶液を5秒で投入した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは1.7から7.0であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.2gを得た。こうして得られた粉末は、平均粒径が13.3μmであり、光散乱強度55.2%、光全透過率91.3%であった。また、化粧料であるファンデーションに配合したところ、従来のマイカ、タルク等の体質顔料を配合したものに比べて、使用感が良好であり、化粧膜の透明性も高かった。

#### 【0019】比較例1

特級試薬 塩化バリウム2.08gと特級試薬 硫酸0.98gをイオン交換水20kgにそれぞれ溶解し、0.0005mol/lのバリウム溶液と0.0005mol/lの硫酸溶液とした。次に、50lの反応槽に硫酸溶液を仕込み、バドルにて200rpmで攪拌、30℃まで加熱後、30℃に加熱したバリウム溶液を60秒で投入した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは3から3であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.1gを得た。こうして得られた粉末は、平均粒径が1.2μmと結晶構造の未発達な微粒結晶であり、光散乱強度31.3%、光全透過率88.7%であった。また、化粧料であるファンデーションに配合したところ、微粒であるため使用感が悪く、伸展性の悪い粉体であった。

#### 【0020】比較例2

特級試薬 水酸化バリウム1.71gと特級試薬 硫酸ナトリウム1.42gをイオン交換水1000gにそれぞれ溶解し、0.01mol/lのバリウム溶液と0.01mol/lの硫酸溶液とした。次に、2lフラスコにバリウム溶液を仕込み、テフロン製バドルにて200rpmで攪拌、100℃まで加熱後、100℃に加熱した硫酸溶液を5分間で滴下した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは1.3で一定であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.2gを得た。こうして得られた粉末は、平均粒径が3.2μmであり、光散乱強度41.9%、光全透過率89.3%であった。また、化粧料であるファンデーションに配合したところ、使用感が悪く、光散乱性の悪い粉体であり、化粧料としては劣っていた。

#### 【0021】比較例3

特級試薬 塩化バリウム2.08gと特級試薬 硫酸0.98gをイオン交換水1000gにそれぞれ溶解し、0.005mol/lのバリウム溶液と0.005mol/lの硫酸溶液とした。次に、5lフラスコに硫酸溶液を仕込み、テフロン製バドルにて200rpmで攪拌、80℃まで加熱後、80℃に加熱したバリウム溶液を10秒で投入した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは2から2であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.2gを得た。こうして得られた粉末は、平均粒径が8.5μmであり、光散乱強度62.4%、光全透過率90.5%であった。また、化粧料であるファンデーションに配合したところ、従来のマイカ、タルク等の体質顔料を配合したものに比べて、使用感が良好であり、化粧膜の透明性も高かった。

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1の硫酸溶液とした。次に、21フラスコに硫酸溶液を仕込み、テフロン製パドルにて200rpmで攪拌。80℃まで加熱後、80℃に加熱したバリウム溶液を15分間で滴下した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは1.6から1.6であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.2gを得た。こうして得られた粉末は、平均粒径が0.5μmと結晶構造の未発達な微粒結晶であり、光散乱強度28.1%、光全透過率89.2\*10

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\*%であったまた、化粧料であるファンデーションに配合したところ、微粒であるため使用が悪く、伸展性の悪い粉体であり、光散乱性にも劣っていた。

【0022】

【発明の効果】本発明によれば、平均粒径が4から20μmと粗大で、光散乱強度が50%以上、かつ、光全透過率が70%以上の物性を有する硫酸バリウムが、安定して製造可能で、かかる粉体は使用感、隠ぺい性に優れ、高い光散乱性と透明性を有する化粧品用体質顔料として有用である。

【手続補正書】

【提出日】平成3年10月7日

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】0013

【補正方法】変更

【補正内容】

【0013】

【実施例】次に実施例及び比較例を挙げて本発明を更に説明する。尚、本実施例及び比較例において、平均粒径及び光散乱強度、光全透過率の評価は以下の如くで行った。

平均粒径

合成された硫酸バリウムスラリーを常温まで冷却し、5℃の濾紙で濾過してイオン交換水で洗浄後、105℃で3時間乾燥して硫酸バリウムの粉末を得る。さらに、この粉末を電子顕微鏡で撮影、結晶の最長部の長さを測定し、その平均値を平均粒径とした。

光散乱強度及び光全透過率

合成された硫酸バリウムを常温まで冷却し、5℃の濾紙で濾過してイオン交換水で洗浄後、105℃で3時間乾燥して硫酸バリウムの粉末を得る。次に、分散媒としてシリコン油を使用し、この硫酸バリウム粉末を20wt%加えて均一に混練し、アプリケーションにより15μmの薄膜をガラス板状に形成させる。さらに、これをヘイズメーター【村上色彩技術研究所製（形式：HR-10 ※

※0）】により、平行光線透過率（Tp）と散乱光透過率（Td）を測定し、 $[Tp + Td]$ を光全透過率、 $[Td / (Tp + Td)] \times 100$ を光散乱強度とした。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0021

【補正方法】変更

【補正内容】

【0021】比較例3

特級試薬 塩化バリウム2.08gと特級試薬 硫酸0.98gをイオン交換水1000gにそれぞれ溶解し、0.01mol/lのバリウム溶液と0.01mol/lの硫酸溶液とした。次に、21フラスコに硫酸溶液を仕込み、テフロン製パドルにて200rpmで攪拌。80℃まで加熱後、80℃に加熱したバリウム溶液を15分間で滴下した。その後、3分間攪拌を続けた後、反応を終了した。反応中のpHは1.6から1.6であった。次いで、常温まで冷却し、5℃の濾紙で濾過してイオン交換水を用いて水洗後、105℃で3時間乾燥して硫酸バリウムの粉末2.2gを得た。こうして得られた粉末は、平均粒径が0.5μmと結晶構造の未発達な微粒結晶であり、光散乱強度28.1%、光全透過率89.2%であったまた、化粧料であるファンデーションに配合したところ、微粒であるため使用感が悪く、伸展性の悪い粉体であり、光散乱性にも劣っていた。

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## CLAIMS

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[Claim(s)]

[Claim 1] A manufacturing method of barium sulfate making a bow rim compound and a sulfated compound react on condition of following (a) - (c).

(a) 0.001-0.1 mol a barium compound solution and a sulfated compound solution of /l, pH of (c) system of reaction which makes drop time which adds either of (b) barium compound solutions and sulfated compound solutions which are made to react by the mole ratios 0.1-5 of a barium compound and a sulfated compound to the other 2 seconds - 7 minutes is set to 0.5-10.

[Claim 2] The manufacturing method according to claim 1 which is one sort as which a barium compound is chosen from barium hydroxide, barium chloride, a barium nitrate, and barium acetate, or two sorts or more, and is one sort as which a sulfated compound is chosen from sulfuric acid, sodium sulfate, sodium hydrogensulfate, and ammonium sulfate, or two sorts or more.

[Claim 3] The manufacturing method according to claim 1 which is what reacts to sulfuric acid by adding barium hydroxide and/or barium chloride.

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] Particle diameter of this invention is large, it is excellent in a using feeling and concealment nature, has high light scattering nature and transparency, and relates to the manufacturing method of barium sulfate useful as an extender for cosmetics.

[0002]

[Description of the Prior Art] Since it is harmless to a human body and concealment nature is strong, barium sulfate is industrially used widely as the contrast medium of X-rays, a gamma ray absorbent, a white pigment, etc. However, when using it for foundation etc. also especially the use as an object for cosmetics, and in it, in conventional barium sulfate, extensibility and adhesion were bad and missing at the using feeling. The transparent feeling was also missing and it had the fault that feeling next to the skin was inferior after makeup. As a means to solve the above-mentioned fault, the way the method of enlarging the particle diameter of barium sulfate makes the crystal form of barium sulfate tabular or needlelike again at JP,62-174238,A is indicated by JP,58-41718,A. However, since heat treatment after compounding these all and mineral acid processing are needed, a manufacturing process is complicated and is not preferred on industrial production. moreover -- general -- generation and its warming of the crystal of barium sulfate -- many research results are reported about the crystal growth by immersion for many years. For example, Bull. Chem. Soc. Japan Vol.27 No.3 According to 121 pages. The result of having carried out observation measurement of the precipitation obtained by mixing barium salt solution and sulfuric acid solution quickly in the large-sized test tube with the electron microscope, The size and shape of particles are governed by the concentration of a mixed raw material, it changes into amorphous, a globular form, a spindle type, a diamond type, etc. variously as concentration becomes thin, and it is shown that the average size of particles changes substantially from 0.013 micrometer to about 2 micrometers. When using barium sulfate

for foundation etc., the using feeling to the coarse particle was preferred, but there was a fault that its reproducibility was bad and its dispersion in particles was remarkable since the generation field of a coarse particle is a very unstable field.

[0003]

[Problem(s) to be Solved by the Invention]Therefore, the purpose of this invention has large particle diameter, and it is in providing the method of manufacturing the barium sulfate which has high light scattering nature and transparency.

[0004]

[Means for Solving the Problem]A result of having inquired wholeheartedly this invention persons solving an aforementioned problem in this actual condition, Conditions, such as reaction raw materials for compounding barium sulfate, reaction mixture concentration, reaction temperature, concentration of common ion, and a reaction operation factor, were clarified in detail and quantitatively, a method of manufacturing stably big and rough barium sulfate which has the light scattering effect corresponding to the above-mentioned purpose, and is transparent was established, and this invention was completed.

[0005]That is, a manufacturing method of barium sulfate of this invention makes a barium compound and a sulfated compound react on condition of following (a) - (c).

(a) 0.001-0.1 mol a barium compound solution and a sulfated compound solution of /l, pH of (c) system of reaction which makes drop time which adds either of (b) barium compound solutions and sulfated compound solutions which are made to react by the mole ratios 0.1-5 of a barium compound and a sulfated compound to the other 2 seconds - 7 minutes is set to 0.5-10.

[0006]It is meltable to solvents, such as water and alcohol, in a barium compound used by this invention, and the barium salt of barium hydroxide and barium chloride, a barium sulfide, a barium nitrate, and barium acetate is mentioned as the example. Before long, barium hydroxide, barium chloride, a barium nitrate, and barium acetate are preferred. Processing of by-products and an ease of acquisition to barium hydroxide and barium chloride which are generated by a reaction are the most preferred. It is meltable to solvents, such as water and alcohol, in a sulfated compound used by this invention, and sulfuric acid, sodium sulfate, sodium hydrogensulfate, ammonium sulfate, potassium sulfate, and lithium sulfate are mentioned as the example. Before long, although sulfuric acid, sodium sulfate, sodium hydrogensulfate, and ammonium sulfate are preferred, sulfuric acid is the most preferred in respect of an ease of acquisition, and a price. These barium compounds and sulfated compounds may be independent respectively, or two or more sorts may be mixed and they may be used.

[0007]Although these barium compounds and sulfated compounds dissolve in solvents, such as water and alcohol, respectively and are used as a barium compound solution and a sulfated compound solution, Barium ion concentration of these barium compound solutions and sulfate ion concentration of a sulfated compound solution require respectively that 0.001-0.1 mol should be /l. When 0.001 mol of such concentration is less than /l, since the degree of supersaturation is low, crystal growth becomes insufficient and big and rough particles are not obtained. In concentration exceeding 0.1 mol /l, since the degree of supersaturation is very large, karyogenesis happens momentarily, and only a super-fine granular crystal which is below a

submicron is obtained. 0.005-0.03 mol of most desirable concentration is /l.

[0008] Addition mole ratios of a barium compound and a sulfated compound are 0.1-5 (barium compound/sulfated compound = 1 / 10 - 5/1).

[0009] Either one of the above-mentioned barium compound solution or a sulfated compound solution is taken to a reaction vessel, and the other is made to react by carrying out a dropping injection in 2 seconds to 7 minutes under stirring as a reaction method. When dropping making time is less than 2 seconds at this time, since it will be in excess saturation suddenly, inside of the system of reaction becomes unstable, rapid karyogenesis is started and a crystal of barium sulfate becomes a super-particle. If dropping making time exceeds 7 minutes, since karyogenesis happens easier than crystal growth since there are very few cores of barium sulfate, and the number of nuclear increases, a coarse particle will be hard to be obtained in the first half of an injection. That is, in order to obtain barium sulfate with big particle diameter, as for drop time, for 2 seconds to 7 minutes is desirable, and especially for 5 seconds to 3 minutes is preferred.

[0010] In that case, it is important to maintain pH of the system of reaction from 0.5 to 10. That is, although various barium compounds and sulfated compounds can be considered as reaction raw materials and barium sulfate is made to any combination, For example, when a barium hydroxide solution is taken to a reaction vessel and the dropping injection of the sulfuric acid solution is carried out in combination of barium hydroxide and sulfuric acid, pH within the system of reaction falls gradually with a dropping injection of a sulfuric acid solution from a state exceeding ten. Thus, light scattering intensity is low and made barium sulfate does not fit the purpose of this invention. When a sulfuric acid solution is taken to a reaction vessel and the dropping injection of the barium fluid is carried out on the other hand, in order that pH within the system of reaction may fulfill the above-mentioned conditions, big and rough barium sulfate particles with high light scattering intensity and light transmittance are obtained. Light transmittance of barium sulfate in which pH is acquired or less by 0.5 becomes low, and is not preferred. Thus, pH of the system of reaction affects light scattering intensity of barium sulfate obtained. Therefore, pH of the system of reaction is one of the important factors [ in / in drop time and reaction concentration / this invention ].

[0011] Although reaction temperature is possible from 60 \*\* to 120 \*\*, as reaction temperature is high, light scattering intensity of barium sulfate obtained also becomes higher. However, since equipment for pressure-proofing is needed above 100 \*\*, not less than 60 \*\* and 100 \*\* or less are desirable. In enforcing a method concerning this invention, unless it deviates from the range of this invention, in a relation with a reactor, a thing of various forms is employable.

[0012] According to this invention, big and rough barium sulfate with a mean particle diameter of 4-20 micrometers can be manufactured. When using it for foundation etc., in mean particle diameter, elongation at the time of spreading worsens in less than 4 micrometers, and a feeling with an umbrella appears. When it exceeds 20 micrometers, it is rough, and admiration becomes strong, and a using feeling is inferior. According to this invention, barium sulfate of not less than 50% of light scattering intensity and not less than 70% of light transmittance is obtained. Light diffusibility is high in light scattering intensity being not less than 50%, and barium sulfate which is excellent in transparency in light transmittance being not less than 70%, and has such

descriptions is useful as an extender for cosmetics.

[0013]

[Example]Next, an example and a comparative example are given and this invention is explained further. In this example and a comparative example, evaluation of mean particle diameter and light scattering intensity, and optical total transmittance was carried out as the following, and was performed.

The barium sulfate by which mean-particle-diameter composition was carried out is cooled to ordinary temperature, and it filters through the filter paper of 5C, dries at 105 °C after washing with ion exchange water for 3 hours, and the powder of barium sulfate is obtained. The length of the longest part of photography and a crystal was measured for this powder with the electron microscope, and that average value was made into mean particle diameter.

Light scattering intensity and the barium sulfate by which optical total transmittance composition was carried out are cooled to ordinary temperature, and it filters through the filter paper of 5C, dries at 105 °C after washing with ion exchange water for 3 hours, and the powder of barium sulfate is obtained. Next, silicone oil is used as carrier fluid, this barium sulfate powder is kneaded to 20wt%, in addition homogeneity, and a 15-micrometer thin film is made to form in the shape of a glass plate by an applicator. It is a hazemeter about this. By [the Murakami Color Research Laboratory make (form :HR-100)], parallel ray transmissivity (Tp) and scattered-light transmissivity (Td) were measured, and optical total transmittance and  $[Td/(Tp+Td)] \times 100$  were made into light scattering intensity for  $[Tp+Td]$ .

[0014]Example 1 reagent chemicals The barium hydroxide 1.71g and reagent chemicals The sulfuric acid 0.98g was dissolved in the ion exchange water 1000g, respectively, and 0.01-mol 0.01 mol was used as the barium fluid of /l with the sulfuric acid solution of /l. Next, the sulfuric acid solution was taught to a 2l. flask, and the barium fluid heated at 100 °C after heating to stirring and 100 °C at 200 rpm with the paddle made from Teflon was thrown in in 30 seconds. Then, the reaction was ended after continuing stirring for 3 minutes. pH under reaction was 1.5 to 7. Subsequently, it cooled to ordinary temperature and filtered through the filter paper of 5C, and using ion exchange water, after rinsing, it dried at 105 °C for 3 hours, and the powder 2.1g of barium sulfate was obtained. In this way, the obtained powder is 11.2 micrometers in mean particle diameter.

They were 69.5% of light scattering intensity, and 91.1% of optical total transmittance.

When blended with the foundation which is cosmetics, compared with what blended extenders, such as the conventional mica and talc, the using feeling was good and the transparency of the makeup film also had it. [ high ]

[0015]Example 2 reagent chemicals Barium fluid and reagent chemicals of 0.02mol /l which were suspended to the ion exchange water 1000g in the barium hydroxide 3.42g The sulfuric acid solution of 0.02mol /l which dissolved the sulfuric acid 1.96g in the ion exchange water 1000g is prepared, Next, the sulfuric acid solution was taught to a 2l. flask, and the barium fluid heated at 100 °C after heating to stirring and 100 °C at 200 rpm with the paddle made from Teflon was thrown in in 2 minutes. Then, the reaction was ended after continuing stirring for 3 minutes. pH under reaction was 1.5 to 7.0. Subsequently, it cooled to ordinary temperature and filtered through the filter paper of 5C, and using ion exchange water, after rinsing, it dried at 105 °C for 3 hours, and the powder 4.5g of barium sulfate was obtained. In this way, the obtained



powder is 4.5 micrometers in mean particle diameter.

They were 60.3% of light scattering intensity, and 88.7% of optical total transmittance.

When blended with the foundation which is cosmetics, compared with what blended extenders, such as the conventional mica and talc, the using feeling was good and the transparency of the makeup film also had it. [ high ]

[0016]Example 3 reagent chemicals The barium chloride 2.08g and reagent chemicals The sulfuric acid 0.98g was dissolved in the ion exchange water 2000g, respectively, and 0.005-mol 0.005 mol was used as the barium fluid of /l with the sulfuric acid solution of /l. Next, the sulfuric acid solution was taught to a 5l. flask, and the barium fluid heated at 80 \*\* after heating to stirring and 80 \*\* at 200 rpm with the paddle made from Teflon was thrown in in 10 seconds. Then, the reaction was ended after continuing stirring for 3 minutes. pH under reaction was 2 to 2. Subsequently, it cooled to ordinary temperature and filtered through the filter paper of 5C, and using ion exchange water, after rinsing, it dried at 105 \*\* for 3 hours, and the powder 2.2g of barium sulfate was obtained. In this way, the obtained powder is 8.5 micrometers in mean particle diameter.

They were 62.4% of light scattering intensity, and 90.5% of optical total transmittance.

When blended with the foundation which is cosmetics, compared with what blended extenders, such as the conventional mica and talc, the using feeling was good and the transparency of the makeup film also had it. [ high ]

[0017]Example 4 reagent chemicals The barium chloride 8.32g and reagent chemicals The sulfuric acid 0.98g was dissolved in the ion exchange water 1000g, respectively, and 0.01-mol 0.04 mol was used as the barium fluid of /l with the sulfuric acid solution of /l. Next, barium fluid was taught to a 2l. flask and the sulfuric acid solution heated at 100 \*\* after heating to stirring and 100 \*\* at 200 rpm with the paddle made from Teflon was thrown in in 30 seconds. Then, the reaction was ended after continuing stirring for 3 minutes. pH under reaction was 7 to 2. Subsequently, it cooled to ordinary temperature and filtered through the filter paper of 5C, and using ion exchange water, after rinsing, it dried at 105 \*\* for 3 hours, and the powder 2.2g of barium sulfate was obtained. In this way, the obtained powder is 6.4 micrometers in mean particle diameter.

They were 61.5% of light scattering intensity, and 87.3% of optical total transmittance.

When blended with the foundation which is cosmetics, compared with what blended extenders, such as the conventional mica and talc, the using feeling was good and the transparency of the makeup film also had it. [ high ]

[0018]Example 5 reagent chemicals The barium hydroxide 1.71g and reagent chemicals The sulfuric acid 0.98g was dissolved in the ion exchange water 1000g, respectively, and 0.01-mol 0.01 mol was used as the barium fluid of /l with the sulfuric acid solution of /l. Next, barium fluid was taught to a 2l. flask and the barium fluid heated at 60 \*\* after heating to stirring and 60 \*\* at 200 rpm with the paddle made from Teflon was thrown in in 5 seconds. Then, the reaction was ended after continuing stirring for 3 minutes. pH under reaction was 1.7 to 7.0. Subsequently, it cooled to ordinary temperature and filtered through the filter paper of 5C, and using ion exchange water, after rinsing, it dried at 105 \*\* for 3 hours, and the powder 2.2g of barium sulfate was obtained. In this way, the obtained powder is 13.3 micrometers in mean particle diameter.

They were 55.2% of light scattering intensity, and 91.3% of optical total transmittance. When blended with the foundation which is cosmetics, compared with what blended extenders, such as the conventional mica and talc, the using feeling was good and the transparency of the makeup film also had it. [ high ]

[0019]Comparative example 1 reagent chemicals The barium chloride 2.08g and reagent chemicals The sulfuric acid 0.98g was dissolved in 20 kg of ion exchange water, respectively, and 0.0005-mol 0.0005 mol was used as the barium fluid of /l with the sulfuric acid solution of /l. Next, the sulfuric acid solution was taught to a 50-l. reaction vessel, and the barium fluid heated at 30 \*\* after heating to stirring and 30 \*\* at 200 rpm with the paddle was thrown in in 60 seconds. Then, the reaction was ended after continuing stirring for 3 minutes. pH under reaction was 3 to 3. Subsequently, it cooled to ordinary temperature and filtered through the filter paper of 5C, and using ion exchange water, after rinsing, it dried at 105 \*\* for 3 hours, and the powder 2.1g of barium sulfate was obtained. In this way, the mean particle diameter of the obtained powder is an underdeveloped particle crystal of 1.2 micrometers and a crystal structure. They were 31.3% of light scattering intensity, and 88.7% of optical total transmittance. When blended with the foundation which is cosmetics, since it was a particle, the using feeling was a granular material whose extensibility it is bad and is bad.

[0020]Comparative example 2 reagent chemicals The barium hydroxide 1.71g and reagent chemicals The sodium sulfate 1.42g was dissolved in the ion exchange water 1000g, respectively, and 0.01-mol 0.01 mol was used as the barium fluid of /l with the sulfuric acid solution of /l. Next, barium fluid was taught to a 2l. flask and the sulfuric acid solution heated at 100 \*\* after heating to stirring and 100 \*\* at 200 rpm with the paddle made from Teflon was dropped in 5 minutes. Then, the reaction was ended after continuing stirring for 3 minutes. pH under reaction was constant at 13. Subsequently, it cooled to ordinary temperature and filtered through the filter paper of 5C, and using ion exchange water, after rinsing, it dried at 105 \*\* for 3 hours, and the powder 2.2g of barium sulfate was obtained. In this way, the obtained powder is 3.2 micrometers in mean particle diameter. They were 41.9% of light scattering intensity, and 89.3% of optical total transmittance. When blended with the foundation which is cosmetics, a using feeling is a granular material whose light scattering nature it is bad and is bad, and was inferior as cosmetics.

[0021]Comparative example 3 reagent chemicals The barium chloride 2.08g and reagent chemicals The sulfuric acid 0.98g was dissolved in the ion exchange water 1000g, respectively, and 0.01-mol 0.01 mol was used as the barium fluid of /l with the sulfuric acid solution of /l. Next, the sulfuric acid solution was taught to a 2l. flask, and the barium fluid heated at 80 \*\* after heating to stirring and 80 \*\* at 200 rpm with the paddle made from Teflon was dropped in 15 minutes. Then, the reaction was ended after continuing stirring for 3 minutes. pH under reaction was 1.6 to 1.6. Subsequently, it cooled to ordinary temperature and filtered through the filter paper of 5C, and using ion exchange water, after rinsing, it dried at 105 \*\* for 3 hours, and the powder 2.2g of barium sulfate was obtained. In this way, the mean particle diameter of the obtained powder is an underdeveloped particle crystal of 0.5 micrometer and a crystal structure. It was with 28.1% of light scattering intensity, and 89.2% of optical total transmittance, and when blended with the foundation which is cosmetics, since it is a particle, use is a granular material whose extensibility it is bad and is bad, and it was inferior also to light scattering nature.

[0022]

[Effect of the Invention]According to this invention, the barium sulfate in which mean particle diameter is as big and rough as 4 to 20 micrometers, light scattering intensity has not less than 50%, and optical total transmittance has not less than 70% of physical properties is stabilized, and it can manufacture, This granular material is useful as an extender for cosmetics which is excellent in a using feeling and concealment nature, and has high light scattering nature and transparency.